The impact of slag fineness on the reactivity of blended cements with high-volume non-ferrous metallurgy slag

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Abstract Non-ferrous metallurgy slags, when highly amorphous, have been shown to behave as supplementary cementitious materials, albeit typically with low reactivity. Due to this feature, high-volume replacement of ordinary Portland cement (OPC) with non-ferrous metallurgy slag is not encouraged. A classical method of increasing slag reactivity is by increasing the fineness of the slag, and this was investigated in the present work. To do so, a non-ferrous metallurgy slag was milled to specific surface areas of 4500 cm²/g and 6500 cm²/g, as determined by the Blaine permeability method. The influence of the fineness on the slag reactivity was investigated using the RILEM R³ isothermal calorimetry procedure. Results demonstrated that the reactivity of these slags was similar to that observed for siliceous fly ashes and increases with slag fineness. Moreover, isothermal calorimetry on blends of OPC with 30, 50 and 70 wt% slag of both finenesses was conducted to investigate the reaction kinetics. A retarding effect of the slag on the Portland clinker hydration was observed, which became more pronounced for higher slag fineness. Finally, mortar compressive strength was tested at 2, 7 and 28 days and compared with the calorimetric results and with thermogravimetric analysis, used to determine the bound water content, at 28 days. At late ages, the increased reactivity for higher slag fineness led to more bound water in hydration products and consequently higher compressive strengths. Moreover, strength gain at later ages due to higher slag fineness might compensate for strength loss due to higher replacement levels. However, at early ages, the strength remained low and increased slag fineness did not yield significant compressive strength enhancement; early strength enhancement likely requires different activation methods.

Keywords: non-ferrous metallurgy slag, supplementary cementitious material, fineness, reactivity

1 Introduction

Non-ferrous metallurgy (NFM) slags may be suitable supplementary cementitious materials (SCMs) from a strength-perspective, as they have been shown to contribute to the compressive strength of blended cements when highly amorphous [1]. However, in contrast to the generally used blast furnace slags of ferrous metallurgy, these non-ferrous metallurgy slags have higher iron contents and lower calcium contents [2] thereby decreasing the reactivity and dissolution rate [3]. Consequently, the NFM slag volumes that can be incorporated in blended cements are usually limited [4].

A typical method of increasing the reactivity of a SCM is by fine grinding in order to increase the specific surface area. Using very fine ground Portland cement, to ensure full hydration, Liu et al [5] showed clearly an increased compressive strength of blended cement pastes with increasing SCM fineness ($d_{50} = 2 - 90 \mu\text{m}$) for various classical SCMs. Moreover, using SCMs with different narrow particle size distributions (PSD), they distinguished a compressive strength increase due to the fineness only, based on inert quartz particles, as well as an increase of the compressive strength due to an increased hydration effect for reactive SCMs at higher fineness, which depends on the SCM type. Such strength increases are also commonly observed in more industrially realistic systems, using commercial cement. For example, Kiattikomol et al. [6] investigated the influence of the fineness ($d_{50} = 2 - 45 \mu\text{m}$)

on the reactivity of a range of fly ashes and reported increased strengths both at early (3 days) and late (90 days) ages for increased fineness. Studies on iron-rich NFM slags have been less extensive, but for example Benkendorff [7] reported that compressive strengths may also be enhanced by increasing the fineness (2800 – 5100 cm²/g) of a lead/zinc slag, similar in composition to the slag used in this work. However, they also reported that grinding too fine might release more Zn from the slag into solution and thereby reduce compressive strength.

In addition to enhancing the reactivity of the SCM, it is known that higher surface areas can have a major, often accelerating, effect on the reaction kinetics of the OPC itself [8, 9]. In particular, Berodier and Scrivener [9] showed, using quartz as an inert filler, that an increased surface area and consequently a smaller interparticle distance enhanced the acceleration rate of the main heat release peak due to silicate (C₃S) hydration measured in isothermal calorimetry. They related this acceleration rate to the nucleation density of C-S-H. Furthermore, the SCM type itself can also have a major impact on the cement hydration [10]. For example the surface of limestone particles is known to promote the nucleation of C-S-H, thereby enhancing the early hydration of cement even more than inert quartz particles [11]. The effect of some iron-rich NFM slags on the cement hydration has been investigated in the past as well. De Schepper et al. [12] and Edwin et al. [13] reported a retarding effect of copper slag on the hydration of cement, which was attributed to the heavy metal content of the slag, in particular Zn, which was present in considerable amounts (> 5 wt%).

In order to distinguish the inherent reactivity of the SCM from its effect on the cement hydration and to obtain quick information on the extent of contribution of an SCM to compressive strength in blended cements, reactivity tests can be used. Recently, a wide variety of reactivity tests for SCMs was compared by the RILEM TC 267-TRM [14]. The R³ (rapid, relevant and reliable) isothermal calorimetry test [15] was found to most closely correlate the reactivity of SCMs, indicated by the cumulative heat release from calorimetry in mimicked pore solution, to the compressive strength of blended cement mortars with those SCMs. Additionally, the technical committee reported values obtained by this test for classical SCMs such as fly ashes and blast furnace slags of ferrous metallurgy. Furthermore, Snellings et al. have recently also reported values for other non-ferrous metallurgical residues [16]. This allows to rank the NFM slag used in this work with respect to other classical or possible future SCMs.

In this work the viability of enhancement of the NFM slag reactivity by increased fineness was studied. The impact of the slag fineness and replacement level on the early cement hydration was investigated. In order to study the inherent slag reactivity, the R³ isothermal calorimetry test was used and the resulting phase assemblage is reported. Finally, compressive strengths on mortars were measured and correlated with the isothermal calorimetry results as well as with the amount of bound water and Ca(OH)₂ in order to explain the observed behaviour.

2 Methodology

2.1 Materials

NFM slag was obtained from an industrial pilot installation after high-temperature treatment and granulation, yielding a highly amorphous slag with a composition and phase assemblage as shown in Table 1 and 2 respectively. The former is obtained from X-ray fluorescence spectroscopy (XRF; S8 TIGER, Bruker) and the latter from X-ray powder diffraction (XRD; D2 Phaser, Bruker). Additionally, a highly amorphous (>95% with ± 4 wt% wüstite, determined using quantitative XRD with zincite as an internal standard) synthetic clean slag with similar composition to the NFM slag but with low amounts of trace elements was available from previous research [17] and was used to clarify the effect of the NFM slag on the hydration kinetics. This slag was synthesised according to a procedure described in detail in previous literature [18]. A powder mixture was heated in an Indutherm TF4000 up to 100 °C above the liquidus temperature. After bubbling a CO/CO₂ gas mixture through the melt to obtain mostly Fe²⁺, it was quenched in water to obtain the high amorphous content. Finally, the slag was milled to a specific surface area of 3872 (±42) cm²/g, as determined by the Blaine permeability method (EN 196-6 [19]). The composition of this synthetic slag was determined by XRF and is reported in Table 1. The FeO content is slightly over the given range of the industrial NFM slag due to leaching of Fe from the steel crucible. The OPC used in this work was a CEM I 52.5N type with a specific surface area of 3478

(± 18) cm^2/g , as determined by the Blaine permeability method (EN196-6 [19]). The Brunauer-Emmett-Teller (BET) specific surface area of this OPC, determined by nitrogen adsorption at 77K (Tristar 3000, Micrometrics), of this OPC is 9967 (± 88) cm^2/g . Prior to the nitrogen adsorption measurement the powder was outgassed at 250 $^\circ\text{C}$ for 13 h. All the chemicals used to prepare the reactivity test (R^3) mixtures, i.e. KOH, K_2SO_4 , $\text{Ca}(\text{OH})_2$ and CaCO_3 , were analytical grade chemicals.

Table 1: Chemical composition in wt% of the NFM slag and the synthetic slag.

Elements	NFM (wt%)	slag	Synthetic slag
FeO	35-45		49.9
SiO₂	25-30		25.4
CaO	15-20		19.3
Al₂O₃	3-6		4.8
MgO	1-2		/
Other	7-12		0.6

Table 2: Phase assemblage of the NFM slag, in wt%.

Phases	Chemical formula	Phase content
Wüstite	FeO	8
Spinel	(Mg, Fe)(Al, Fe, Cr) ₂ O ₄	11
Quartz	SiO ₂	<1
Undetected/ Amorphous	/	80

2.2 Methods

The NFM slag was milled to specific surface areas of 4533 (± 28) cm^2/g and 6491 (± 49) cm^2/g , as determined by the Blaine permeability method (EN 196-6 [19]), using high-intensity milling in a stirred media mill. The slags are coded as “Bl 4500” and “Bl 6500” for the least and most fine slag, respectively. The resulting particle size distribution (Fig. 1) of the raw materials was also measured using laser diffraction (LS 13 320, Beckman Coulter) on dry powders. The optical parameters for OPC were $n = 1.73$ and $k = 0.1$, similar to [20]. As there are no literature values for the optical parameters for the slag, the refractive index was calculated as $n = 1.72$ using the Gladstone-Dale model using values for the oxides tabulated in Young and Finn [21]. For the imaginary coefficient, k , a similar value was taken as for OPC, $k = 0.1$, after making sure this did not introduce an overtly large fraction of particles $< 1 \mu\text{m}$. This yields a d_{50} of 11.79 μm , 9.17 μm and 4.70 μm for OPC, Bl 4500 and Bl 6500, respectively. Additionally, the BET specific surface area of the milled slags was determined as described for OPC before and yielded a specific surface area of 12239 (± 95) cm^2/g and 18373 (± 127) cm^2/g for Bl 4500 and Bl 6500 respectively.

Figure 1: Cumulative particle size distribution of the raw materials.

Both a reference pure cement paste and blended cement pastes, replacing OPC with 30, 50 and 70 wt% of NFM slag with both finenesses, were prepared by mixing the solid powders with water to obtain a liquid/solid (L/S) mass ratio of 0.4. The replacement levels were chosen in order to observe evolutions of or differences in fineness effects when replacing medium to high amounts of OPC with the NFM slag. Additionally, OPC was replaced with 70 wt% of the synthetic slag and mixed with water to obtain a L/S mass ratio of 0.4 as well. These pastes were investigated using isothermal calorimetry (TAM Air, TA instruments) at 20 °C for 7 days in order to record the reaction heat during hydration. The heat flow and cumulative heat of hydration of the blends is reported from 1 hour after mixing to avoid taking into account the influence of introduction of the ampoules to the channels. It should be noted that this also means that the initial heat due to wetting and initial dissolution is not taken into account and not discussed in the results.

To elucidate the effect of the NFM slag on the early hydration kinetics, the pore solution of the pastes was investigated by using ICP-OES (720-ES, Varian inc.) on the supernatant liquid after centrifugation of the pastes at 7000 rpm for 5 min. Immediately after centrifugation and before the measurement, the liquid was filtered using a 0.45 µm filter and acidified using a 3% HNO₃ solution to avoid any precipitation.

The R³ isothermal calorimetry reactivity test was conducted on model mixes as described in [14]. In this reactivity test, a solid mix is prepared as 22.22 wt% slag (as SCM), 66.66 wt% Ca(OH)₂ and 11.12 wt% CaCO₃. This solid is mixed in a L/S mass ratio of 1.23 with a solution composed of 97.66 wt% H₂O, 0.39 wt% KOH and 1.95 wt% K₂SO₄, mimicking the pore solution after the Ca(OH)₂ starts dissolving. The materials were kept at 40 °C prior mixing, and 15 g of the paste was subsequently used for isothermal calorimetry (TAM Air, TA instruments) measurements at the same temperature (40 °C). Additionally, the resulting phase assemblage of the R³ mixes after 7 days at 40 °C was investigated using XRD (D2 Phaser, Bruker) after stopping the hydration of the crushed paste with solvent exchange. This solvent exchange was done by immersion (30 sec stirred, 5 min unstirred) in isopropanol (2x) and diethyl ether (1x) followed by drying for 8 min at 40 °C.

Furthermore, blended cement pastes were hydrated for 28 days and then investigated using thermogravimetric analysis (TGA; TGA/SDTA851, Mettler Toledo) on crushed pastes where the hydration was stopped by solvent exchange as described before. TGA was conducted from 30 °C to 980 °C in inert atmosphere (100 ml/min N₂) with a heating rate of 10 °C/min. The amount of bound water was calculated from the weight loss between the initial weight at room temperature and the weight at 550 °C, which assumes all isopropanol or diethyl ether was removed in the drying step of the solvent exchange. The Ca(OH)₂ content in the paste was determined from the weight loss in the 350-450 °C region. The tangential method was used to determine the water loss due to dehydroxylation of Ca(OH)₂. In this method it is assumed that the weight loss due to the water released from C-S-H continues linearly over the region of the weight loss due to Ca(OH)₂ dehydroxylation. The water loss only attributable to Ca(OH)₂ is then obtained from the difference at the inflection point between lines tangential to the weight loss curve before and after this weight loss region.[22]

Finally, mortars with 30, 50 and 70 wt% slag of either fineness in the solid binder were prepared and tested in compressive strength as described in EN196-1 [23], although with a water over binder mass ratio of 0.4 for a more direct comparison with the paste results. At each testing age (2, 7 and 28 days) the strength activity index (SAI) was calculated by taking the ratio (in %) of the compressive strength of the blended cement mortars over the compressive strength of the reference OPC mortars.

3 Results and discussion

3.1 Early reaction kinetics

The effect of the slag content on the heat flow during early hydration (Fig. 2a) shows a clear decrease of the main hydration peak with increasing slag content. Considering that this peak is typically attributed to the dissolution of C₃S and the formation of C-S-H, this decrease can be explained by the decreased OPC content as the maximum of the heat flow decreases linearly with the OPC content (R² > 0.999) for both slag finenesses, with approximately 0.14 J/(h*g solid) and 0.15 J/(h*g solid) per replaced wt% OPC for Bl 4500 and Bl 6500 respectively. At later ages (20-25 h) there is a shoulder which can be attributed

to the renewed dissolution of C_3A [24]. With increasing slag content, this shoulder appears to become more pronounced. Presently the exact cause for this effect is still being debated in literature. A closer investigation on quartz blended systems by Berodier [8] reported an enhancement of this shoulder, even though the quartz is considered to behave as an inert filler, and related the enhancement to rapid C_3A dissolution as a consequence of lower sulphate presence in the pore solution, which would inhibit that dissolution. An enhancement of the shoulder could also be observed in the work of Quennoz and Scrivener [25] in a C_3S+C_3A +gypsum model paste when a higher C_3S /gypsum ratio was used, where the increased amount of C-S-H was considered to adsorb a higher amount of sulphate. Moreover, Quennoz and Scrivener [26] proposed that the acceleration rate of the peak of pure C_3A hydration is related to the available C_3A surface for dissolution and phase nucleation. In the case of pure C_3A hydration this peak refers to the formation of AFm phase. However, the behaviour of the secondary aluminate peak in OPC hydration is very similar, such as the increased delay and broadening of this peak with higher sulphate content [27]. Hence the heat release from renewed C_3A dissolution and accelerated ettringite formation may have a similar underlying cause. Thus, the lower amount of sulphate in the pore solution with decreasing OPC content may also lead to higher availability of the C_3A surface for dissolution and ettringite nucleation, as less of the surface is blocked by remaining sulphate adsorption, and thus increase the reaction rate as well. Considering the low sulphate content of the slag (< 0.5 wt%) and lower sulphate concentration in the pore solution of the blended cement (Table 3) a similar effect most likely leads to the more pronounced shoulder in this case.

At even later times (>40 h) there is another broad shoulder, more clearly seen after normalizing the heat flow to the OPC content (Fig. 3a), which is likely related to AFm formation [25]. Finally, after several days the slag starts reacting, yielding increased heat flows for 30 and 50 wt% replacement of OPC with respect to pure OPC hydration, shown in Fig. 2a at the end of the measurement (150-168 h). While the replacement of OPC by 70 wt% slag does not lead to a heat flow increase per gram solid at these ages, the heat flow normalized to the OPC content is higher (Fig. 3a), showing also slag reaction in this mix. Despite the extra heat flow from the slag reaction, the cumulative heat after 7 days (Fig. 2b) clearly decreases with increasing slag content, as the slag reaction does not make up for the decreased heat release from the lower OPC content.

Figure 2: Heat flow (a) and cumulative heat release (b) per gram solid during hydration of OPC blended with non-ferrous metallurgy slag (low fineness, B1 4500). The insert in (a) shows a zoomed in view of the heat flow at later times.

The comparison of the heat flow normalized to the OPC content is presented in Fig. 3a for the blended cements with the highest amount of slag (70 wt% slag, 30 wt% OPC) as the differences are most pronounced there and similar to the effects seen at other replacement levels. The replacement of OPC by NFM slag leads to a delay in the onset of the reaction from 3.75 h for OPC to 4.12 h for a 30-70 OPC-slag (low fineness) blend. Moreover, with increased fineness, the onset of reaction increases further to 4.62 h. The onset of reaction is defined here similarly to Schöler et al. [10] as the intersection of the horizontal line through the minimum of the induction period and the best fit through the inflection point of the acceleration stage of the main hydration peak. In addition to the retardation of the onset of hydration, the acceleration rate and the maximum heat release of the main hydration peak decreases with

increasing slag content and fineness. The decrease of the acceleration rate with increasing slag content and fineness indicates that the effect of the NFM slag cannot be described by simple behaviour inert particles would exhibit, as this behaviour is the reverse of that observed for inert quartz particles by Berodier and Scrivener [9]. Considering the acceleration rate was linked to the nucleation of C-S-H particles, a decreased acceleration rate might indicate inhibition of C-S-H nucleation on the surface of the slag. Moreover, the NFM slag used in this work contains 7-12 wt% of various residual elements, among which are several elements which can retard cement hydration, even in small quantities, such as Zn [28]. If these elements would leach out of the slag in the early hydration period, they might cause the retarding effect of the slag, which would be larger at higher slag fineness. Therefore, a synthetic, clean slag, i.e. without any significant amount of trace metals, and with similar composition to the original slag (Table 2) was blended with OPC in a 30-70 wt% OPC-slag ratio and the heat flow during hydration was measured (Fig. 3b). The clean slag shows a similar behaviour to the original slag (Bl 4500) and it can be concluded that the residual elements in the original slag are most likely not the (main) cause of the retarding effect of the slag. It should be noted that the clean slag had a slightly lower specific surface area ($3872 \pm 42 \text{ cm}^2/\text{g}$) which likely accounts for the slightly decreased retardation when using this slag, though a small part may still be caused by the lack of residual elements. Considering this result, other effects are most likely causing the retardation.

In fly ashes a similar retarding effect is sometimes observed [10, 29] and authors have explained this in different ways. Fajun et al. [29] reported decreased Ca^{2+} contents in the pore solution and suggested that the fly ash surface acts as a Ca^{2+} sink by chemisorption, thereby delaying C-S-H and $\text{Ca}(\text{OH})_2$ precipitation. In contrast, Schöler et al. [10] found higher Ca^{2+} contents in the pore solution of fly ash blended cements. In addition, they reported increased aluminium levels in the pore solution of fly ash-containing blended cements and attributed the retardation to the hindering effect of aluminium on C_3S dissolution [30] and C-S-H nucleation. Considering the similarity in behaviour of these NFM slags with that in the aforementioned literature for fly ashes and their similarity in reactivity, which is discussed in section 3.2, an investigation into the pore solution at early age is warranted. Therefore, the pore solution after 2 h of the reference OPC and of a blended cement with high volume (70 wt%) NFM slag with the high fineness ($6491 \text{ cm}^2/\text{g}$) were collected and the major elements were measured (Table 3). Due to the lower amount of OPC, also the concentrations of K, Na and S are considerably lower in the blended cement with respect to the reference. A rough estimate of the OH^- concentration can be obtained from a charge balance calculation, as all positive charges (mainly Na^+ , K^+ and Ca^{2+}) have to be counteracted by negative charges (mainly SO_3^{2-} and OH^- , but also Al was taken into account as $\text{Al}(\text{OH})_4^-$, considering the high pH). While the other elements will also contribute (e.g. Fe, Si), their contribution is much smaller (typically $< 1 \text{ mmol/l}$ [31]) and will not significantly change the conclusions from the calculations. Moreover, the calculated values are in the range of expected values from literature [31]. As a consequence of the lower alkali concentrations in the blended cements, also the OH^- concentration (and thus pH) is lower. Additionally, it is clear that neither of the theories proposed above can explain the retardation effect of the slag on the OPC hydration as the Ca and Al concentration in the pore solution of the blended cement are higher and lower respectively.

Table 3: Measured concentrations of the major and relevant elements in the pore solution after 2 hours of hydration of the reference cement (OPC) and a blended cement with 30 wt% OPC and 70 wt% NFM slag with a fineness of $6491 \text{ cm}^2/\text{g}$ (Bl 6500).

Element (mmol/l)	Ca	K	Na	S	Al	OH^-^c
OPC	25	165	62	66	0.0018 ^a	144
Bl 6500	30	41	26	19	0.0008 ^b	87

^ameasured intensity was ± 10 times the intensity in the blank. ^bmeasured intensity was ± 5 times the intensity in the blank.

^cestimated OH^- concentration calculated from a charge balance equation using the reported values where Al is considered as $\text{Al}(\text{OH})_4^-$ due to the high pH of the pore solution. Note that this calculation only takes into account the major elements, and the calculated OH^- concentration should thus only be considered qualitatively.

The increase in fineness also appears to lead to a less pronounced shoulder due to renewed C_3A dissolution in the 20-25 h region, as discussed before. Since the slag contains around 0.5 wt% SO_3 , this decreased enhancement might be explained by higher release of sulphates from the slag due to the higher surface area, thereby slightly increasing inhibition of C_3A dissolution. On the other hand, the shoulder

due to conversion of ettringite to AFm phase(s), around 40 h, appears to grow, possibly indicating increased formation of AFm phases. Considering the high (calculated) OH^- concentration, and thus pH, already reached after 2 h (Table 3), the most reactive part of the slag may have started reacting at this point [32], which would explain the growth of this shoulder by increased Al and Fe release from the slag.

Finally, at late ages, the heat release normalized to the OPC content increases by addition of the slag as well as by increasing the fineness of the slag (Fig 3a). The former shows the reactivity of the slag, while the latter indicates the expected reactivity enhancement due to the fineness increase.

Figure 3: Heat flow per gram OPC: comparison of blends with 30 wt% OPC and 70 wt% slag with (a) different fineness or (b) with and without (“clean”) trace elements.

Due to the increase of the retarding effect of the slag with increasing slag fineness, the cumulative heat released by OPC replacement with fine slag (Fig. 4a) is lower until the paste has hydrated for 3 days. Afterwards, the inherent slag reactivity increase with higher fineness leads to higher cumulative heat release, increasingly so with higher slag content. At the lowest slag content (30 wt%), the cumulative heat is statistically the same for both finenesses though the difference is expected to grow at later ages.

3.2 Inherent slag reactivity

The inherent slag reactivity was confirmed by the R^3 calorimetry test (fig 4b), where the finer slag (BI 6500) showed higher cumulative heat release, both after 3 and 7 days as the effect of the slag on C_3S and C_3A hydration is neglected in this model system which does not contain OPC. Comparison of the values obtained in the R^3 reactivity test (table 4) with literature values for classical SCMs [14] shows that the values, and thus the reactivity, most closely resemble those obtained for siliceous fly ashes (table 4), which are already commonly used in the cement and concrete industry.

Figure 4: Cumulative heat released, measured using isothermal calorimetry in the first 7 days (a) per gram OPC in the blended cement pastes and (b) per gram SCM from the R^3 pastes.

Table 4: Cumulative heat of the R³ model systems comprising slag of different fineness and comparison with literature data of fly ashes. Standard deviations in brackets, based on 2 measurements.

SCM	SCM fineness (cm ² /g)	Cumulative heat after 3 days (J/g SCM)	Cumulative heat after 7 days (J/g SCM)
NFM Slag	4500	117.4 (±4.9)	200.7 (±5.3)
	6500	161.9 (±8.3)	239.8 (±11.0)
Fly Ash 1 ([14], “SFA I”)	4420	81.6	162.5
Fly Ash 2 ([14] “SFA E”)	6910	119.6	214.1

The phase assemblage after the R³ reactivity test was investigated in order to determine the preferential phases as a consequence of the slag reaction as well as the effect of the increased fineness. The detected phases (Fig 5, focused on the most interesting regions) are ettringite, portlandite, C-S-H (present as a broad peak underneath the calcite peak at $\pm 29.4^\circ$; $d = 3.03 \text{ \AA}$) and AFm phases. The determination of the exact type of AFm phases is difficult as the peak position can shift depending on the anion, and possible solid solutions [33], as well as hydration state [34]. The main AFm peak in these diffractograms, around 11.9° ($d = 7.43 \text{ \AA}$) can be ascribed to either Al-monocarbonate ($d = \pm 7.6 \text{ \AA}$ [33, 35, 36]) or, considering the high Fe content of the slag, to Fe-hemicarbonate ($d = \pm 7.48 \text{ \AA}$ [36]). It should be noted that the behaviour of Fe in these iron-rich blended cements is presently not yet well understood. The phase assemblage is almost identical for both slag finenesses and no new peaks are detected when the slag fineness is increased. While there might be a small increase in the amount of ettringite, this is limited and the majority of the extra heat release is most likely due to the formation of X-ray amorphous phases.

Figure 5: Phase assemblage of the R³ model mixes after 7 days hydration at 40 °C. E = Ettringite, AFm = AFm phases, P = portlandite, C = calcite, C-S-H = calcium-silicate-hydrate.

3.3 Compressive strength

Compressive strengths and SAIs of the mortars, are presented in Figure 6. It is clear that the strength increases with time and OPC content. After 28 days compressive strengths of the blended cements with medium to low slag content (50 wt% or less) reach SAIs higher than the OPC content, indicating contribution of the slag to the strength, as expected from the calorimetry results and R³ reactivity tests. Moreover, there is a clear effect of the fineness at later ages (> 7 days), which is more distinct for a slag content of 50 wt%. In fact, increasing the slag fineness from ± 4500 to $\pm 6500 \text{ cm}^2/\text{g}$ allows an increase of the slag content from 30 wt% to 50 wt% while keeping the strength approximately equal, making the slag fineness a suitable tool to tailor the late age strength as slag fineness and replacement level appear to be interchangeable in this region. However, at early ages (2 days) there is no significant strength increase due to increased slag fineness. At high slag content, the strength may even decrease slightly. This can be linked to the calorimetry results, where the cumulative heat for this blend is lower for a finer slag until after 3 days of hydration. In general, the lack of strength increase at early age is most likely related to the lack of significant reaction of the slag at these ages in combination with the retarding effect of the slag on the hydration of the cement phases.

Figure 6: Compressive strength and strength activity indices (SAI) of mortars. Error bars indicate the standard deviation.

Using TGA the amount of $\text{Ca}(\text{OH})_2$ and bound water after 28 days can be determined, where the former is important for the pozzolanic reaction while the latter gives an indication of the amount of hydrated phases that are present in the binder. After normalization of the $\text{Ca}(\text{OH})_2$ and bound water content, as determined by TGA, to the OPC content (fig 7a), the effect of the slag can be more closely investigated. With increasing slag content, the amount of bound water normalized to OPC increases, as reported before [1], showing the contribution of the slag to the hydration products. Moreover, increasing the fineness also increases the normalized amount of bound water, indicating enhanced formation of hydration products which explains the increased strengths after 28 days. While there is an increase in the bound water content, the $\text{Ca}(\text{OH})_2$ content normalized to OPC stays relatively constant. As the slag contains a significant amount of CaO , this will also be dissolved and contribute in the hydration reactions. Nevertheless, for blends with high contents of fine (BI 6500) slag, a decrease in the $\text{Ca}(\text{OH})_2$ content is observed most likely due to the higher slag reactivity which consumes more $\text{Ca}(\text{OH})_2$ in the pozzolanic reactions.

Correlating the bound water content and $\text{Ca}(\text{OH})_2$ content with the compressive strength (Fig 7b) reveals that the former correlates well, while the correlation with the latter is poor, due to consumption of $\text{Ca}(\text{OH})_2$ in the (strength-enhancing) pozzolanic reactions. Since the $\text{Ca}(\text{OH})_2$ is not expected to give significant contribution to strength and is being consumed in the pozzolanic reactions, the correlation of the bound water with the strength improves further by subtracting the water bound in $\text{Ca}(\text{OH})_2$ from the total bound water, to account only for the water bound in hydrated cement phases, in particular water bound in C-S-H. Consequently, this property can be used to qualitatively compare the expected compressive strength of different blended cements while only requiring a small amount of SCM.

Figure 7: (a) Bound water and $\text{Ca}(\text{OH})_2$ content at 28 d, as determined by TGA, normalized to the OPC content. The estimated relative error is 10%. (b) Correlation of the bound water content or $\text{Ca}(\text{OH})_2$ content with the compressive strength. Error bars are not shown for clarity.

In both figures: BW = bound water content, CH = Ca(OH)_2 content and BW-CH = bound water content excluding water from Ca(OH)_2 .

4 Conclusions

The heat of hydration of OPC blended with non-ferrous metallurgy slag and the influence of the specific surface area of the slag on the reactivity in these systems was investigated. Heat release of blended cement pastes at early ages revealed decreasing reaction heat with increasing slag content. Additionally, a retarding effect of the slag on the hydration of the cement phases was observed which could not be explained by several common theories for similar behaviour in fly ashes nor by the heavy metal content. The R^3 isothermal calorimetry reactivity test showed that the slag was similar in reactivity to siliceous fly ashes, commonly used in concrete, and that increasing the fineness yields a more reactive slag. However due to the retarding effect of the slag and limited slag reaction at early age, the early strength did not significantly improve by increasing the slag fineness. In contrast, at later ages compressive strength did increase significantly with slag fineness due to the increased formation of hydration products and for a sufficiently high OPC content (> 50 wt%); an increased slag fineness can compensate for an increase in replacement level. Therefore, enhancement of the early age strength should be an important aim in further research. Additionally, the retarding effect of the slag on cement hydration at early age requires further elucidation.

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